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## MULTI-LAYER PLASTIC CONTAINER

BACKGROUND OF THE INVENTION

5 This invention relates to thermoformed multilayer structures having at least one layer of a blend of an amorphous polyamide polymer having a  $T_g$  greater than about  $120^\circ\text{C}$  with an aliphatic polyamide polymer and at least one layer of a structural thermoplastic polymer.

Containers and films with good gas barrier properties are needed for the packaging of perishable items such as foods, drinks, pharmaceuticals and cosmetics. Amorphous polyamides have been shown to  
10 possess both excellent oxygen barrier properties and optical properties and are therefore desired to be used in conjunction with other, often less expensive, structural materials, e.g., as in a multilayer film or container. Containers and films containing such amorphous polyamides can be made by thermoforming processes. For the purpose of this invention, thermoforming processes include any process for forming a shaped article (e.g., a film or a container) which is performed in a process which (a) is distinct from the  
15 initial melt processing step and (b) which is performed at a temperature which is elevated but substantially lower (e.g., by at least about  $30^\circ\text{C}$ ) than that required in the melt processing step. These thermoforming processes are performed on a semi-finished shaped article (often called a "preform") which was cast or molded from a molten polymer. Thus, for example, extrusion of a film would not be a thermoforming process according to this invention because it is a melt processing step; vacuum-forming the film to  
20 prepare a container would be a thermoforming process. Examples of thermoforming processes include thermoforming as the term is commonly used, (but excluding melt phase thermoforming), vacuum-forming, solid phase pressure forming, co-injection blow-molding, co-injection stretch blow-molding, tube extrusion followed by stretching, scrapless forming, forging and tubular or flat sheet oriented film processes. Examples of articles that can be prepared using thermoforming processes are films and containers such as  
cups, bottles, trays, dishes and bowls.

DETAILED DESCRIPTION OF THE INVENTION

The amorphous polyamides useful in this invention are those which are lacking in crystallinity as shown  
5 by the lack of an endotherm crystalline melting peak in a Differential Scanning Calorimeter test (ASTM D3417) and whose glass transition temperatures (T<sub>g</sub>) are greater than about 120°C. (T<sub>g</sub> is measured according to ASTM D-3418 and is the average of onset and endset temperature.) The amorphous polyamides of this invention are prepared from aliphatic diamines and aromatic di-acids. Examples of aliphatic diamines which can be used to prepare the amorphous polyamides are: hexamethylenediamine,  
10 2,2,4-trimethyl hexamethylene diamine, 2,4,4-trimethyl hexamethylenediamine, 2-methyl pentamethylene diamine, bis-(4-aminocyclohexyl)-methane, 2,2-bis-(4-aminocyclohexyl)-isopropylidene, 1,4-(1,3)-diamino cyclohexane, 1,5-diaminopentane, 1,4-diaminobutane, 1,3-diaminopropane and 2-ethyl diaminobutane. Examples of aromatic dicarboxylic acids which can be used to prepare the amorphous polyamides are: isophthalic acid, terephthalic acid, and alkyl substituted iso-or terephthalic acid.

15 Specific examples of polyamides which can be used in the containers of this invention include: hexamethylenediamine isophthalamide, hexamethylenediamine iso/terephthalamide, and mixtures of 2,2,4- and 2,4,4-trimethyl hexamethylenediamine terephthalamide. Preferred are the hexamethylenediamine iso-terephthalamides with ratios of iso-to tere-in the range of about 60/40 to 100/0. Most preferred are such polymers with ratios of iso-to tere-of about 70/30. Small amounts (0 to 5 mole% based on diamine) of 4,4-  
20 bis(aminocyclohexyl)methane may be incorporated in the polyamide. Other additives such as slip additives and thermal stabilizers may also be used.

The semicrystalline aliphatic polyamides used in this invention include addition polymers of amino acids, such as nylon 6, nylon 66, nylon 6,10 and nylon 6,10, and condensation polymers of hexamethylenediamine with dibasic acids such as succinic, adipic and sebacic acids. Copolymers and  
25 terpolymers of these aliphatic polyamides may also be used; e.g., copolymers of hexamethylene-diamine/adipic acid with caprolactam. To achieve a blend with amorphous polyamide with good optical properties, the aliphatic polyamide should preferably have a ratio of nitrogen to carbon atoms of at least 0.12, preferably at least 0.14.

co-and terpolymers of ethylene with vinyl acetate, acrylic acid or methacrylic acid, and ionomers obtained by partially neutralizing such acid copolymers.

In the multilayer structures of this invention, it may often be desirable to interpose between said first layer of polyamide blend and said second layer of structural thermoplastic polymer a resin having adhesion to both such layers. Many adhesive resins are known in the art which would serve this purpose. In general, such adhesive resins are thermoplastic polymers having carbonyl groups derived from functional groups of free carboxylic acids, carboxylic acid salts, carboxylic acid esters, carboxylic acid amides, carboxylic anhydrides, carbonic acid esters, urethanes, ureas or the like. In these thermoplastic polymers, the carbonyl group concentration may be changed in a broad range, but in general, it is preferred to use a thermoplastic polymer containing carbonyl groups at a concentration of 10 to 1400 millimoles per 100 g of the polymer, especially 30 to 1200 millimoles per 100 g of the polymer. Suitable adhesive resins include polyolefins modified with at least one ethylenically unsaturated monomer selected from unsaturated carboxylic acids and anhydrides, esters and amides thereof, especially polypropylene, high density polyethylene, low density polyethylene and ethylene-vinyl acetate copolymers modified with at least one member selected from acrylic acid, methacrylic acid, crotonic acid, fumaric acid, itaconic acid, maleic anhydride, itaconic anhydride, citraconic anhydride, ethyl acrylate, methyl methacrylate, ethyl maleate, 2-ethylhexyl acrylate, acrylamide, methacrylamide, fatty acid amides and imides of the acids described above. U.S. 4,230,830, the disclosure of which is hereby incorporated by reference, discloses resins particularly suitable for use with nylons. In addition, as the adhesive resin, there can be used ethylene-acrylate copolymers, ionomers, polyalkylene oxide-polyester block copolymers, carboxymethyl cellulose derivatives, and blends of these polymers with polyolefins.

The multilayer structures of this invention have a minimum of two layers, the first layer of polyamide blend and the second layer of structural thermoplastic resin. In some cases the structures have a third layer of an adhesive resin. The structures may also have five or more layers, e.g., two outer layers of the structural thermoplastic resin, an inner layer of the polyamide blend, two or more layers of adhesive resin, and other inner thermoplastic resin layers as desired.

By virtue of the incorporation of the layer of amorphous polyamide, the multilayer structures of this invention have excellent barrier properties. The oxygen permeability of the layer of amorphous polyamide

The film samples so prepared were thermoformed on a sheet vacuumformer Model 222, made by the Brown Machine Company of Beaverton MICH. The mold was for making 96 mm diameter and 38 mm deep cups. To thermoform the sheet samples they were preheated in a heating chamber equipped with infrared radiant heaters. The heating time was determined by the temperature of the film sample, which was measured with Thermolabels, made by the Paper Thermometer Company of Greenfield, New Hampshire. These labels have an adhesive backing and are attached to the film sample adjacent to the area to be thermoformed. When the desired temperature was reached, preheating was terminated by moving the sample sheet into the mold position followed by the automatic activation of the mold. If the preheat temperature was too low, the force provided by the vacuum was not sufficient, and no or very little forming was accomplished. The lowest temperature at which the cup could be almost completely formed was defined as the lower temperature limit of thermoformability (LTLT) for a given structure. The LTLT of the film made with Sample A was measured to be 110 deg C. The LTLT of the film made with the unmodified amorphous polyamide was measured to be 143 deg C.

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### Example 2

Three layer films were coextrusion cast, with a core layer selected from Sample A of Example 1, from the unmodified amorphous polyamide of Example 1, and from Sample B, a blend of 80 weight % of the amorphous polyamide of Example 1 and 20 weight % nylon 6,12 (condensation copolymer of HMDA and dodecanoic acid). The core layer was approximately 0.075 mm thick, extruded with a 25 mm extruder at 10 rpm and 216 deg C melt temperature. Surface layers were polypropylene (PP), each approximately 0.25 mm thick. The structures were cast at a velocity of 1m/min. and cooled by two 300 mm diameter chill rolls cooled with 70 deg C circulating water. Since the adhesion between the nylon and the PP surface layers was nil, they could be readily separated and the PP layers discarded. The residue was a series of single layer films of the nylon or nylon blends which were made under coextrusion conditions.

Tensile tests performed on these film samples at elevated temperatures show that the yield strengths.

Both controls are the unmodified amorphous polyamide of Example 1. Cast film samples were 0.05 to 0.10 mm thick. Testing was done in the machine direction.

**Table 2**

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	<u>Core Layer Composition</u>	<u>Haze, %</u>	<u>OPV</u>	<u>Tg, C</u>
10	Unmodified amorphous polyamide	12.9	20.8	123
	Sample A	8.8	21.2	99
15	Sample B	77.2	25.7	118

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(Haze measured by ASTM D-1003; OPV in cc.mil/sqm.Day.Atm and measured by ASTM D-3985; Tg measured by ASTM D-3418 and is the average of onset and endset temperatures)

The data for Sample B indicate that it would not be satisfactory for use in applications where good optical properties are desired.

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**Example 3**

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Samples C, D, E and F were prepared by mixing the components shown in Table 3, and melt blending the mixture in a 25 mm diameter single screw melt processor (extruder), working at 100 rpm speed and with a melt temperature between 260 and 282 deg C. The samples were extruded into a strand at a rate between 2.2 and 4.5 lb/hr, cooled in water and cut into pellets.

Example 4

Samples G and H were prepared by mixing pellets of the components recited in Table 4. Using these samples, the unmodified amorphous polyamide of Example 1, or unmodified nylon 6 as one of the surface layers, three layer coextruded films were prepared. The equipment and process described in Example 1 was used. The other surface layer in these films was a low density polyethylene with a melt index of 4.5. The polyethylene was extruded on the 38 mm extruder at 20 rpm, with a melt temperature of 235 deg C. The overall thickness was 0.175 mm, with the polyamide layer comprising approximately 0.075 mm of the total. The third layer was the adhesive used in Example 1.

The coextruded film samples were thermoformed according to the procedure described in Example 1. The LTLT values for each sample were determined and are shown in Table 4, along with the optical properties and oxygen permeabilities of the films. Also presented in the table are the glass transition temperatures of the polyamide layer.

Table 4

<u>Composition</u>	<u>Haze</u>	<u>OPV</u>	<u>LTLT</u>	<u>T<sub>g</sub></u>
Unmodified amorphous polyamide (PA)	24.2	7.9	132	128
80/20 PA/Nylon 6	23.3	8.4	82	100
80/20 PA/Nylon 66.6	23.0	8.7	93	98



2. A thermoformed multi-layer structure of Claim 1 where said amorphous polyamide is a hexamethylenediamine isophthalamide with a ratio of iso-to tere-phthalamide in the range of about 60/40 to 100/0.

3. A thermoformed multi-layer structure of Claim 1 where the ratio of nitrogen to carbon atoms in said  
5 semicrystalline aliphatic polyamide is at least 0.12.

4. A thermoformed multi-layer structure of Claim 3 where said semicrystalline aliphatic polyamide is selected from nylon 6, nylon 66.6, nylon 6,10 and copolymers thereof.

5. A thermoformed multi-layer structure of Claim 1 where the blend in said first layer comprises 60-90%, preferably 70-85%, amorphous polyamide and 10-40%, preferably 15-30%, semicrystalline aliphatic  
10 polyamide.

6. A thermoformed multi-layer structure of Claim 1 where said structural thermoplastic resin has a Tg of less than about 110°C.

7. A thermoformed multi-layer structure of Claim 1 where said structural thermoplastic resin is selected from polyethylene terephthalate, polystyrene, polyvinyl chloride, linear and branched polyethylenes, co-and  
15 terpolymers of ethylene with vinyl acetate acrylic acid or methacrylic acid, and ionomers obtained by partially neutralizing such acid copolymers.

8. A thermoformed multi-layer structure of Claim 1 in which a layer of adhesive resin is interposed between said first layer and said second layer.

9. A method for preparing a shaped multi-layer structure having excellent gas barrier properties  
20 comprising casting or molding from molten polymers a semi-finished, multi-layer shaped article comprising a layer of a blend of one or more amorphous polyamides having a Tg greater than about 120°C and one or more semicrystalline aliphatic polyamides and at least one layer of a structural thermoplastic resin, and thermoforming said semi-finished article at a temperature below 125°C to prepare said shaped multi-layer structure.

25 10. A method of Claim 9 where said amorphous polyamide is a hexamethylenediamine isophthalamide with a ratio of iso-to terephthalamide in the range of about 60/40 to 100/0.

11. A method of Claim 9 where the ratio of nitrogen to carbon atoms in said semicrystalline aliphatic

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## EUROPEAN SEARCH REPORT

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EP 88 10 4826

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	EP-A-0 104 436 (FELDMÜHLE AG) * Claims; page 5, lines 20-26; page 6, lines 11-23; page 8, lines 3-22; page 12, lines 26-33; page 15, lines 4-27 * ---	1-14	B 29 C 51/14 B 32 B 27/08 B 32 B 27/34 C 08 L 77/06
A	GB-A-2 023 088 (TOYO SEIKAN K. LTD) * Claims * ---	1	
A	US-A-4 079 850 (TOYO SEIKAN K. LTD) * Claims * -----	1	